CIC NEWSLETTER

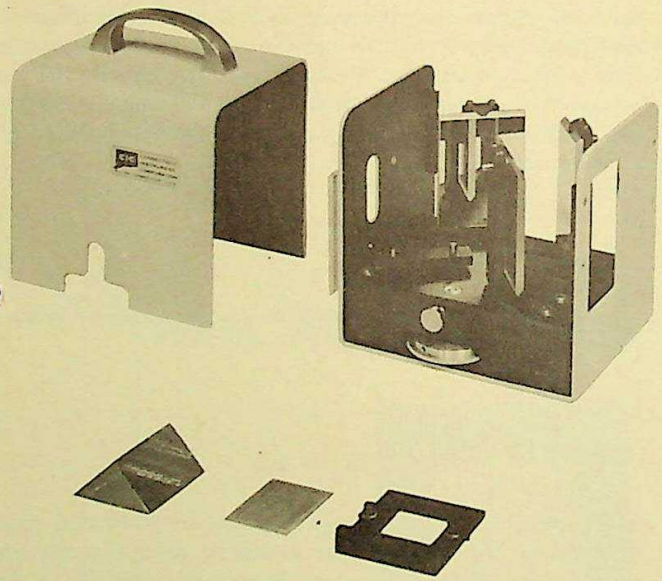
Published bimonthly by
Connecticut Instrument Company
Division of Barnes Engineering Company
Wilton, Connecticut

NUMBER 14 September, 1961

ATTENUATED TOTAL REFLECTION— A NEW INFRARED SAMPLING TECHNIQUE*

FOR SOLIDS, FILMS AND STRONGLY ABSORBING LIQUIDS

By PAUL A. WILKS, JR.



Every once in a while a new infrared sampling technique comes along that makes possible the analysis of still another group of samples by infrared spectroscopy. The development of KBr pellets and the introduction of new infrared transmitting materials are examples. The recently published work of J. Fahrenfort on attenuated total reflection appears to be of equal consequence to the spectroscopist.

We have been studying the technique for the past several months to determine possible applications and to find, if possible, a practical method of obtaining ATR spectra on conventional infrared equipment. The results of our efforts to date are given in the article at left and the first commercially available Attenuated Total Reflection attachment pictured above. This attachment is by no means the ultimate in ATR equipment but the spectroscopist will find it highly versatile and ideal for experimentation in this most promising new infrared technique.

The principles of Attenuated Total Reflection have been developed by J. Fahrenfort in a paper presented at the 1959 Meeting in Bologna and later at the Gordon Conference.

He gives a very complete mathematical explanation of the phenomenon which will not be repeated here. For the benefit of those who may not be familiar with the ATR effect, we will show a graphical explanation which is oversimplified but adequate for our purposes.

Assume that a beam of radiation is passed into a prism so that it is totally reflected from the back face, as in Figure 1.

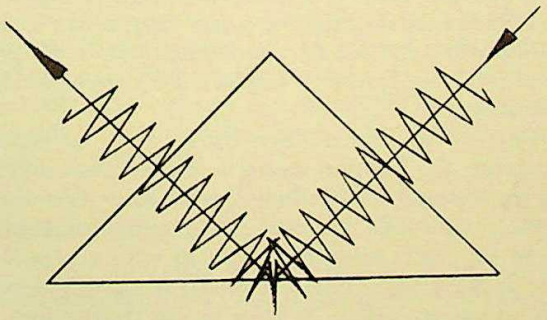


Figure 1.

It has been shown, both mathematically and by physical measurements, that some portion of the energy of the beam escapes from the totally reflecting face and then is returned into the prism. It is almost as though the ray had a wave front of a finite width and behaved as shown in the diagram.

continued on page 2

*Presented at the 1961 Ohio State Symposium on Molecular Structure and Spectroscopy.

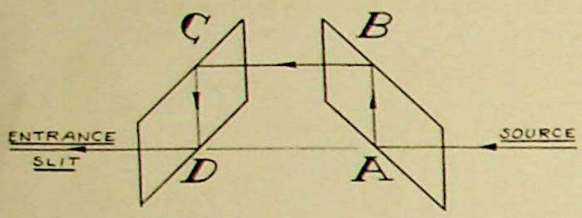


Figure 2.

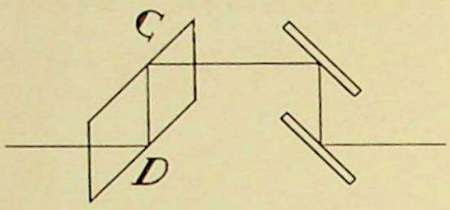


Figure 3.

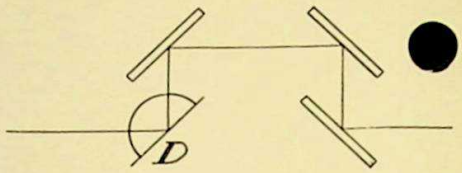


Figure 4.

continued from page 1

It would appear that, if an absorbing material is placed in contact with the reflecting surface, the energy that escapes temporarily from the prism would be selectively absorbed, much as in a transmission spectrum. Under the proper conditions this is indeed the case.

The absorption-like spectra obtained by this method have two important and unique features:

1. The band intensities are the equivalent of an extremely shallow (5 microns or less) penetration into the sample.
2. They are completely independent of the sample thickness.

As manufacturers of infrared cells, it comes as a considerable relief to find a sampling procedure that eliminates precise and extremely short pathlengths as a requirement for infrared sampling!

Because of these characteristics, it is apparent that the ATR technique will have widespread application in the infrared analysis of solid materials and other strongly absorbing substances.

From a practical standpoint, therefore, we have set out to develop a simple optical system that may be mounted in any conventional infrared spectrophotometer. The principal requirement of the system is that a reflecting surface be available from which the sample beam is reflected at the proper angle of incidence. It is quite helpful if the angle of incidence can be varied.

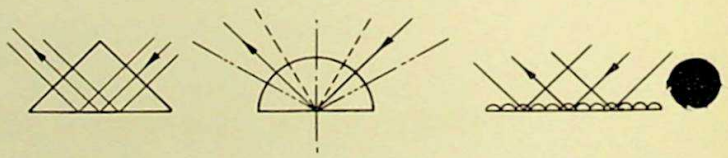
We have considered three systems, each of which is quite useful. The first one, shown in Figure 2, was suggested to us by workers of the Shell Development Company in Emeryville, California. The two double prisms are fashioned from an infrared transmitting material with a high index, such as Irtran-2, Silver Chloride, KRS-5 or CsBr. The sample can be placed at A, B, C or D or at any combination. The system will produce quite satisfactory ATR spectra although it has the disadvantage of having a fixed angle of incidence and also it requires a fair amount of expensive crystal.

A simplification of this system is shown in Figure 3. Here two mirrors replace one of the double prisms. This is somewhat less expensive, but it still has a fixed angle of incidence.

The system in Figure 4 is the one we finally settled upon. The angle of incidence on mirror D can be varied over a wide range. Also, considerable freedom of sampling procedure is permitted.

Now that we have an optical system, the next problem is to mount the sample in such a way that the ATR effect can be obtained. Here the requirement is that the sample be in close contact with the reflecting surface.

This can be done easily if the sample can be deposited on the reflecting surface by evaporation, thermosetting, spraying or some similar way. The reflecting plate may be a prism or half cylinder, as shown in Figure 6a. However, these forms require considerable amounts of expensive crystal. Except for Irtran-2, most of the materials are soft and subject to damage by repeated usage. The third form, shaped like a coderoy or grooved plate, shown in Figures 6b and c, has been worked out to provide an inexpensive yet effective ATR plate. Silver chloride can be easily pressed into this form with a proper die. After pressing, the sample may be deposited as above. Or, if the sample is solid, the AgCl plate may be formed and pressed on it in the same operation in a KBr press.



a *b* *c*

Figure 5

A number of representative spectra are shown on page 4. Although they appear quite similar to absorption spectra, they are not identical. They are just as characteristic of the molecule, however.

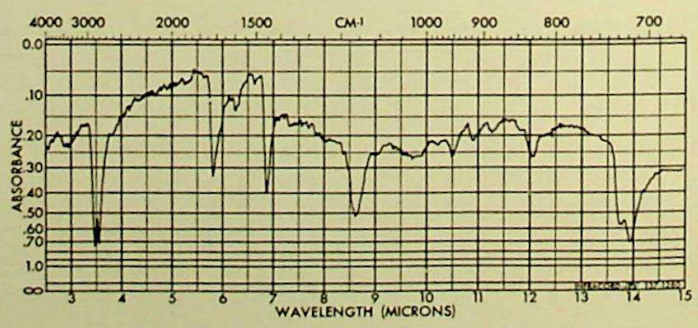
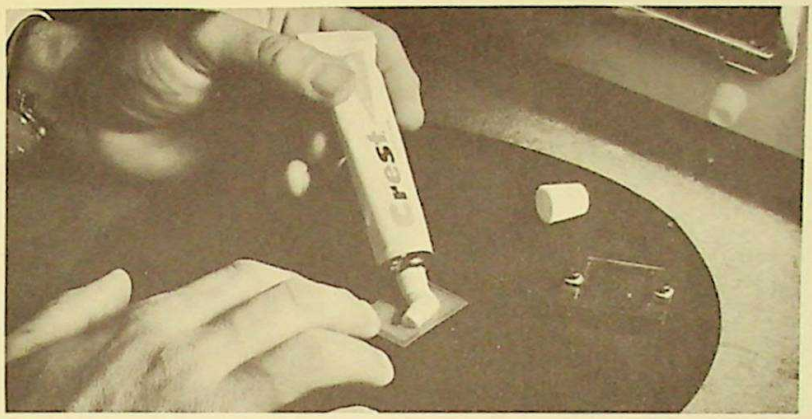
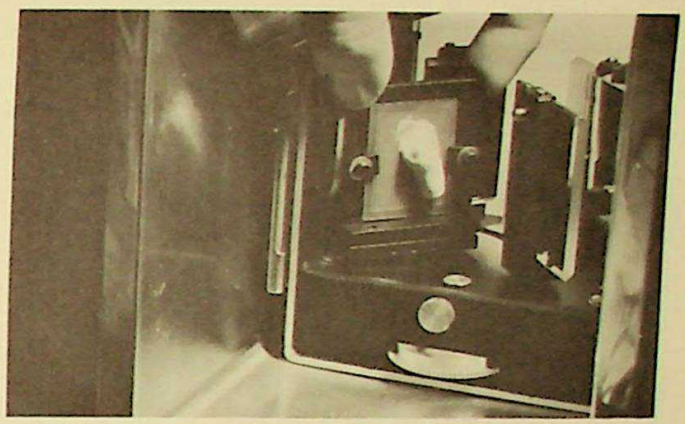


Figure 6

We feel that we have just begun to scratch the surface of applications and sampling approaches of this new technique. From what little we have done so far, we are quite enthusiastic over its potential in the infrared examination of solids and other strongly absorbing materials.

ATR-1 ATTENUATED TOTAL REFLECTANCE ATTACHMENT





A typical example of the technique: At left, the sample is spread on the pressed AgCl plate (in this case, tooth paste). At right, the plate holder is placed on the ATR attachment. See page four for the resulting spectrum.

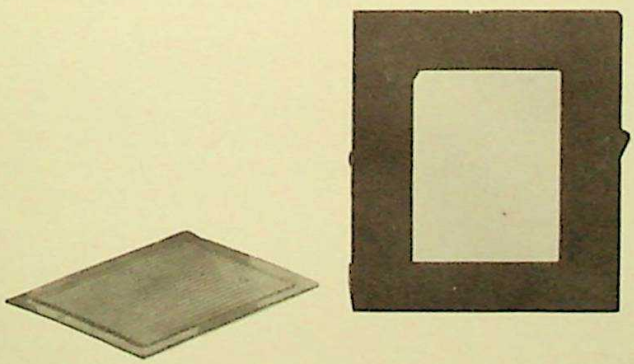
The Model ATR-1 attachment has an adjustable angle of incidence at the sample point permitting a variation of from 50° to 20°. Several different sampling methods (see below) are possible with the attachment.

The unit slips quickly into the cell slide of most commercial instruments. The Model ATR-1 is designed so that it may be used either singly or in pairs (one in each beam) so that differential or compensated spectra may be obtained.

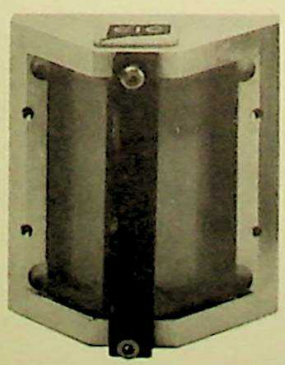
The price of the Model ATR-1 attachment, including an AgCl reflector plate holder and six pressed AgCl disposable reflector plates, is $300.00. This unit may be used on all Perkin-Elmer and Beckman infrared spectrophotometers.

A kit consisting of the ATR-1 unit, 6 AgCl plates, one AgCl solid holder and one AgCl liquid cell is priced at $600.00

THREE ATR SAMPLING METHODS NOW AVAILABLE



Reflector Plate and Holder



Solid Holder

Liquid Holder

Disposable Reflector Plates

There are many applications in ATR sampling where it is desirable to cast or evaporate a sample on the reflecting surface. The disposable reflector plates are economical enough so that one may be used once (or a few times, if the sample is easily removed) and then discarded. They are pressed from AgCl and are available from C.I.C. already pressed for a price of $3.00 each.

Solid Sample Holder

This unit consists of a reflecting prism mounted in a clamping device that permits a solid sample to be held in close contact with the reflecting surface. Prisms of AgCl, KRS-5 and Irtran-2 are available for use with the holder. Prices are as follows:

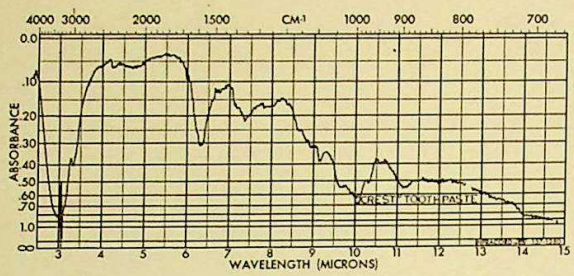
ATR Solid Sample Holder (excluding prism)	$50.00
AgCl Prism	100.00
KRS-5 Prism	200.00

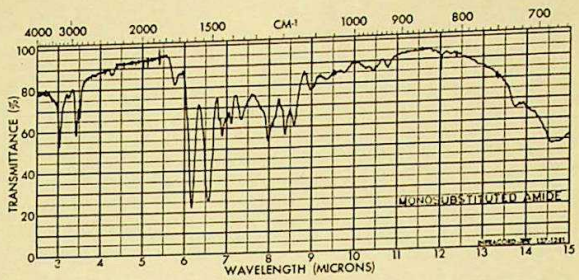
Liquid Sample Holder

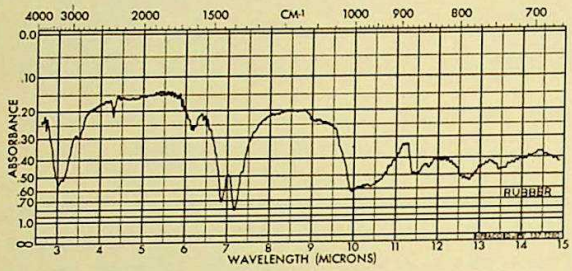
For liquid sampling by the ATR technique, the Liquid Sample Holder is available. It consists of a glass body to which a reflecting prism is clamped with a Teflon "O" ring. The same prisms as the Solid Sample Holder are usable with the Liquid Sample Holder.

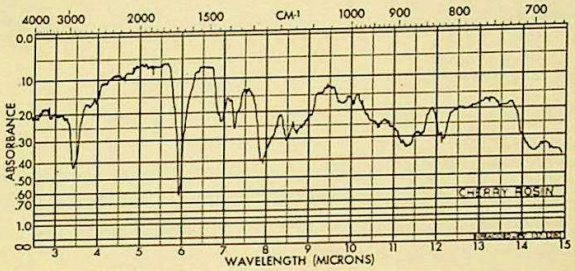
ATR Liquid Sample Holder (excluding prisms)	$50.00

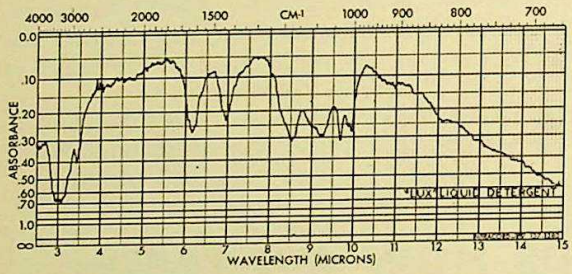
TYPICAL APPLICATIONS OF ATTENUATED TOTAL REFLECTANCE

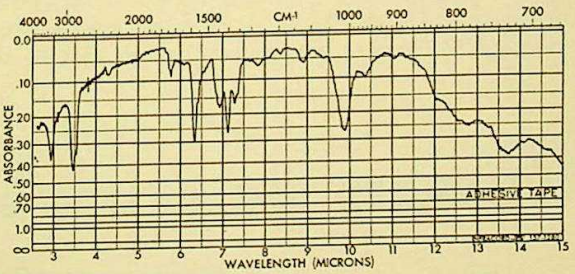


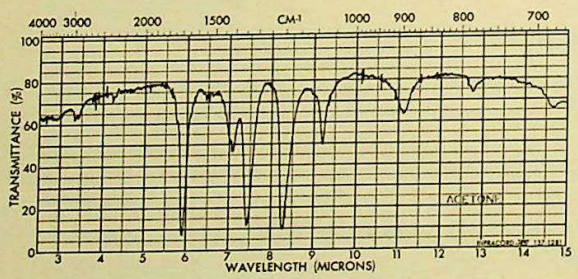












ACKNOWLEDGMENT

We are indebted to a number of people for helpful suggestions and encouragement in this program. Among them are Dr. J. Fahrenfort and spectroscopists of the Shell Development Company in Emeryville, California, and the Du Pont Polychemicals Laboratory in Wilmington, Delaware.

Connecticut Instrument Company
Division of Barnes Engineering Company
Wilton, Connecticut

Bulk Rate
U.S. Postage
PAID
Wilton, Conn.
Permit No. 30